

Unified Equations of State for Ozone-Safe Refrigerants R32 and R125¹

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ABSTRACT

Unified equations of state for gaseous and liquid difluoromethane (R32) and pentafluoroethane (R125) were compiled. The coefficients of the equations were determined on the basis of the experimental data on density and heat capacities c_v and c_s . At compiling the equations the satisfaction of Maxwell's rule was ensured. The equations describe the thermodynamic properties of R32 and R125 at temperatures from 140 to 433 K and from 178 to 480 K correspondingly at pressures up to 70 MPa with experimental precision. In particular, the root-mean-square deviations of the calculated values of density from the most reliable experimental data are equal 0.10% for R32 and 0.12% for R125.

KEYWORDS: difluoromethane; equation of state; gas; liquid; pentafluoroethane.

1. INTRODUCTION

Necessity of the replacement of the traditional refrigerants depleting atmospheric ozone on alternative refrigerants caused an intensive study of properties of such substances. Difluoromethane (R32) and pentafluoroethane (R125) are perspective ozone-safe refrigerants. The data on their thermodynamic properties are necessary for designing refrigerating plants using difluoromethane or pentafluoroethane or their mixtures with other substances as working media.

Recently the unified equations of state for R32 and R125 [1, 2] are published. However at their compiling the newest p, ρ, T -data [3] were not used. The fulfilled comparison showed that in general these equations of state describe data [3] satisfactorily, however the errors of their analytical description for each substance are still higher than the errors of the experiments. It should be noted that the data [3] cover the wide range of temperature and pressure and the number of experimental points are more than the quantity obtained in all previous researches. So we decided to compose new equations of state for R32 and R125 taking into account the data [3].

2. EQUATIONS OF STATE

The compiled in this work equations of state have the form

$$\frac{F(\omega, \tau)}{RT} = \alpha_0(\omega, \tau) + \alpha(\omega, \tau), \quad (1)$$

where $F(\omega, \tau)$ is the free Helmholtz energy, $\omega = \rho/\rho_{cr}$ is the reduced density, $\tau = T/T_{cr}$ is the reduced temperature. The first term of the equation (1) is an ideal-gas part that is determined on the basis of data on heat capacity c_{p0} . The function $\alpha(\omega, \tau)$ is a real part of the equation of state and can be written as

$$\alpha(\omega, \tau) = \sum_{i=1}^m \sum_{j=0}^{r_i} a_{ij} \frac{\omega^i}{\tau^j} + \exp(-\omega^2) \sum_{i=1}^n \sum_{j=1}^{s_i} b_{ij} \frac{\omega^i}{\tau^j}, \quad (2)$$

Coefficients a_{ij} and b_{ij} are determined on the basis of the experimental data on thermodynamic properties of compressed gas and liquid.

The equation of state in the form (1) was effectively used for analytical description of data on thermodynamic properties of a number of substances, including difluoromethane [2, 4, 5].

At compiling the unified equations of state for R32 and R125 p, ρ, T -data for gaseous and liquid phases listed in Table 1 and Table 2 were used. Besides the experimental data for the single-phase region the calculated values of saturated vapor and liquid densities and saturated vapor pressure were used. The equations for calculation of those values exactly reproducing the experimental data were taken from the work [1] for both refrigerants. Use of the calculated values of the properties for the saturation line is involved both with small amount of experimental data on density of saturated vapor and with necessity to have values of ρ' , ρ'' and p_s at the same temperatures in order to ensure the satisfaction of Maxwell's rule.

For qualitative representation of caloric properties of difluoromethane 73 experimental values of isochoric heat capacity c_v in the temperature range from 153 to 341 K at pressures 5,2 – 32 MPa and 101 values of saturated heat capacity c_s in the temperature range 141 – 342 K [15] were included in the set of used data. The satisfaction of Maxwell's rule was ensured by use of the values of ρ' , ρ'' and p_s from the set of p, ρ, T -data for the saturation line given on 41 isotherms in the temperature range 140 – 340 K.

At composing the equation of state for R125 99 experimental values of heat capacity c_v in the temperature range from 200 to 342 K at pressure from 3.8 to 33 MPa and 93 values of heat capacity c_s in the temperature range 176 – 278 K [15] were also used. To ensure the satisfaction of Maxwell's rule 31 values of ρ' , ρ'' and p_s from the basic set of p, ρ, T -data in the temperature range from 180 to 330 K were used.

The values of isobaric heat capacities of ideal gas which were necessary for use of the information on heat capacities c_v and c_s at compiling the equation of state were taken as average values between data [16, 17] for R32 and [1, 18] for R125. These values were approximated by polynoms (3) and (4) correspondingly

$$c_{p0}/R = 4.3914 - 2.5143\tau + 5.3885\tau^2 - 1.6057\tau^3, \quad (3)$$

$$c_{p0}/R = 2.9072 - 11.5586\tau + 2.1135\tau^2, \quad (4)$$

At approximation of experimental data the values of their weights were taken into account. The weights were assumed to be equal inverse proportional to dispersions of data and calculated according to the method [19]. The values of relative deviations δp used at the calculation of the weights of p, ρ, T -data are shown in the next to last column of Table 1 for R32 and Table 2 for R125. The values of the errors of data on heat capacities c_v and c_s and data used for satisfaction of Maxwell's rule were assumed to be equal $\delta c_v=0.5\%$, $\delta c_s=0.7\%$ and $\delta p_s=0.1\%$ for both substances. The accuracy and the mutual agreement of the data and also the density of information for each property influenced the choice of these values.

A step-wise regression analysis method [20] was used for determining the coefficients of the equation (2) for both R32 and R125. The method is based on minimization of the square functional formed on the basis of the approximated data. In this method the number of used coefficients of the equation increases from minimum

given to optimum by means of adding the statistically most significant terms chosen from the empirical bank of terms of equation. These terms are determined at each stage of calculations in accordance with the taken significance level of the Student criterion. The Fisher criterion is used to determine if the current equation significantly improved the quality of approximation of the data in comparison with the previous one. If the improvement is significant, a new term is added to the equation. Otherwise the equation is taken as final.

The bank of terms used at compilation of both equations of state contained 70 terms in polynomial part ($m=10$, $r=6$) and 50 terms in exponential one ($n=10$, $s=5$). Reliable approximation of data in a wide range of parameters was ensured by assigning the value 0.05 to the significance level of the Student criterion and the value 0.25 to the level of the Fisher criterion.

As pointed above different data are included into minimized functional. Therefore it was complicated gradually by including step by step p, ρ, T -data for the single-phase region and for the saturation line, data ensuring satisfaction of Maxwell's rule and data on heat capacities c_v and c_s . This kind of method of calculations allows to estimate a mutual agreement of different data and to find better assigned values of the relative errors used for calculating weights.

The coefficients of the final equations of state obtained with taking into account of all above listed properties are shown in Tables 3 and 4. During calculations the following values of the critical parameters and gas constants were assumed

For R32 $T_c = 351.35 \text{ K} [1]; \rho_c = 427.00 \text{ kg/m}^3 [1]; R = 159.821 \text{ J/(kg}\cdot\text{K)}$.

For R125 $T_c = 339.33 \text{ K} [1]; \rho_c = 571.29 \text{ kg/m}^3 [1]; R = 69.275 \text{ J/(kg}\cdot\text{K)}$.

3. COMPARISON THE EXPERIMENTAL DATA

The results of the comparison of the initial experimental data for both substances with the calculated by means of the equations of state are shown in the last column of Table 1 for R32 and Table 2 for R125 where the root-mean-square deviations δp_m for each author are shown. It should be noted that for 6 points from the work [3] for R32 and 9 points from the same work for R125 which are in the critical region, where the values of derivative $\partial p / \partial p$ are very big, values of root-mean-square deviations for pressure δp_m are given in Tables 1 and 2. At comparison with the data for the saturation line the calculated values of density and of saturated vapor pressure were determined on the basis of Maxwell's rule.

On the results of calculations the histograms of deviations δp for R32 and R125 were built. They are shown in the Figure1 (a and b). It can be seen from the figure that the distribution of deviations is close to normal. During building the histograms 6 points for R32 and 9 points for R125 lying in the critical region and having deviations δp higher than 1% (while deviations δp are 0.03 – 0.24%) have not been taken into account. Also 18 points for R32 and 21 points for R125 that have deviations with absolute values in the range 0.5 – 1% are not included in the histograms but they were taken into account at calculating the shown values $\delta p_m = 0.10\%$ (for 1946 points) and 0.12% (for 1668 points).

For R32 additional comparison with p, ρ, T -data [21, 22] not used at compilation of the equation of state showed that corresponding values of the root-mean-square deviations δp_m are 0.24% and 0.13% (for 123 points in temperature range 243 – 373 K and pressure range 0.1 – 4.8 MPa and for 95 points at 290 – 370 K and 0.1 – 6.5 MPa correspondingly).

Root-mean-square deviations of the initial values of saturated vapor [1] and experimental data on heat capacities c_v and c_s [15] from the values calculated from the equation of state for R32 are equal 0.16%, 0.31% and 0.85% correspondingly. Taking into account the errors of the pointed data the deviations can be considered to be quite satisfactory. It also should be noted that after exclusion of the value -0.72% at the minimum temperature 140 K where the vapor pressure is small (82 Pa) the value δp_{sm} decreases to 0.12%.

For R32 the experimental data of saturated vapor pressure [7, 8, 15, 22 - 28] and density of saturated vapor [7, 24, 28] and liquid [7, 8, 24, 26, 28] are also compared with the values calculated by means of the equation of state. These data cover the temperature range 140 – 351 K for p_s , 219 – 345 K for ρ'' and 139 – 346 K for ρ' and the numbers of points in the corresponding sets are 327, 55 and 87. For the majority of authors root-mean-square deviations of data on pressure p_s and density ρ' from the values calculated from the equation of state on the basis of Maxwell's rule are not higher than 0.2%. For data [15] and [23] given in the temperature ranges 140 – 180 K and 149 – 245 K the values of δp_s are 1.36% and 0.92% correspondingly. That is caused by big relative errors of the experimental data in the region of low pressure. It should be noted that deviations of the data [15] and [23] from the calculated by us have different signs. The majority of the data on density of saturated vapor have more significant deviations than data on density of saturated liquid. The values of $\delta \rho''_m$ lie mainly in the range 0.7 – 1% and only for data [7] $\delta \rho''_m = 0.13\%$. But the accuracy of the experimental values of ρ'' are as a rule lower than the values of ρ' .

For the new experimental data [3] of saturated vapor pressure covering the interval $T = 223 - 351$ K (139 points) the value of δp_{sm} is equal 0.04%. Comparison

with values of densities of saturated liquid and vapor obtained by extrapolation the p, v, T -data [3] to the saturation line showed that the root-mean-square deviations for 41 points in temperature range 140 – 340 K are $\delta\rho'_m = 0.04\%$ and $\delta\rho'' = 0.38\%$.

A comparison of calculated values of speed of sound for R32 with experimental data [29, 30] was fulfilled also. For 120 points [29] covering temperature range 243 – 373 K and pressure range 0.27 – 33 MPa the root-mean-square deviation δw_m is equal 0.56%. For 305 points [30] presented at temperatures 248 – 343 K and pressures 1.7 – 65 MPa the value δw_m is 0.70%.

For R125 additional comparison with p, ρ, T -data [31, 32] showed that corresponding values of the root-mean-square deviations $\delta\rho_m$ are 0.26% and 0.43% (for the total amount of 56 points in temperature range 383 – 424 K and pressure range 0.9 – 11 MPa). Such values of deviations are caused by the disagreement of data [31, 32] with those used at compilation of the equation of state.

Root-mean-square deviations of the initial values of saturated vapor [1] and experimental data on heat capacities c_v and c_s [15] from the values calculated by means of the equation of state for R125 are equal 0.07%, 0.45% and 0.29% correspondingly.

For R125 experimental data of saturated vapor pressure [8, 12 – 15, 26 – 28, 31 – 33] and density of saturated vapor [14] and liquid [8, 11, 26, 28] are also compared with the calculated values. These data cover the temperature range 180 – 338 K for p_s , 275 – 320 K for ρ'' and 173 – 336 K for ρ' and the numbers of corresponding points are 393, 10 and 54. For the vast majority of authors root-mean-square deviations of data on pressure p_s and density ρ' from the calculated values are not higher than 0.2% and 0.1% correspondingly. The value of $\delta\rho''_m$ for data [14] is equal 0.32%.

For the experimental data [3] of saturated vapor pressure presented at temperatures 222 – 339 K (98 points) the value of δp_{sm} is 0.08%. Comparison with values of ρ' and ρ'' obtained by extrapolation the p, v, T -data [3] to the saturation line showed that the root-mean-square deviations for 31 points at temperatures 180 – 330 K are $\delta \rho'_m = 0.02\%$ and $\delta \rho'' = 0.31\%$.

A comparison of calculated values of speed of sound for R125 with experimental data [34, 35] showed that for 72 points [34] for gaseous phase covering temperature range 273 – 343 K and pressure range 0.01 – 0.24 MPa the root-mean-square deviation δw_m is equal 0.07%. For 167 points [35] for liquid phase at temperatures 241 – 333 K and pressures 0.32 – 32 MPa the value δw_m is 0.54%.

After compiling the unified equations of state for R32 and R125 we received the monograph [36] where analogous equations are published. The fulfilled comparison showed that the equations [36] describe the most reliable p, v, T -data [3, 6 - 9, 11, 14] with root-mean-square deviations 1.3 – 2 times higher than the deviations presented in Tables 1 and 2. It can be explained by the fact that the number of coefficient in the equations [36] is less than in the equations compiled by us.

4. CONCLUSION

The values of thermal, caloric and acoustic properties of R32 and R125 calculated by means of compiled unified equations of state were compared with the experimental data. The detailed comparison showed that these equations describe the most reliable experimental data with high precision. Therefore the new unified equations of state may be used for calculation of thermodynamic properties of gaseous and liquid difluoromethane and pentafluoroethane in a wide region of temperatures and pressures.

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Table 1. List of p, ρ, T -data used at compilation of the equation of state for R32 and root-mean square deviations $\delta\rho_m$ of the experimental values of density from the calculated ones.

Year	Authors	Range of parameters.		Numb. of points	$\delta\rho$,	$\delta\rho_m$,
		T , K	p , MPa		%	%
1993	Holst [6]	150 – 375	1.5 – 72	126	0.1	0.14
1994	Defibaugh and co-auth.[7]	243 – 373	0.3 – 9.8	379	0.1	0.12
1996	Magee [8]	142 – 396	3.8 – 35	135	0.03	0.03
1996	Zhang and co-auth.[9]	290 – 370	0.1 – 6.5	81	0.1	0.10
1997	de Vries [3]	224 – 433	0.02 – 20.6	1143	0.05	0.08
		349 – 352	5.5 – 5.9	6	0.5	0.09*
1995	Outcalt, McLinden, ρ'' [9]	140 – 340	$8 \cdot 10^{-5}$ – 4.6	41	0.1	0.17
1995	Outcalt, McLinden, ρ' [9]	140 – 340	$8 \cdot 10^{-5}$ – 4.6	41	0.05	0.03

* For 6 points belonging to the critical region the value of $\delta\rho_m$ is presented.

Table 2. List of p, ρ, T -data used at compilation of the equation of state for R125 and root-mean square deviations $\delta\rho_m$ of the experimental values of density from the calculated ones.

Year	Authors	Range of parameters.		Numb. of points	$\delta\rho$,	$\delta\rho_m$,
		T , K	p , MPa		%	%
1991	Zausaev and Kletsky [10]	273 – 443	0.6 – 6.1	43	0.1	0.23
1992	Defibaugh and co-auth.[11]	275 – 369	1.6 – 6.3	150	0.1	0.16
1993	Holst [12]	180 – 480	0.2 – 68	211	0.1	0.17
1995	Ye and co-auth. [13]	290 – 390	0.1 – 3.6	93	0.1	0.14
1995	Boyes and Weber [14]	273 – 363	0.3 – 4.6	80	0.05	0.05
1996	Magee [8]	178 – 398	3.6 – 35	77	0.03	0.02
1997	de Vries [2]	243 – 413	0.02 – 19.8	952	0.05	0.08
		339 – 341	3.6 – 3.8	9	0.5	0.13*
1995	Outcalt, McLinden, ρ'' [9]	180 – 330	$6 \cdot 10^{-3}$ – 3.0	31	0.1	0.34
1995	Outcalt, McLinden, ρ' [9]	180 – 330	$6 \cdot 10^{-3}$ – 3.0	31	0.05	0.07

* For 9 points belonging to the critical region the value of $\delta\rho_m$ is presented.

Table 3. Coefficients a_{ij} and b_{ij} of the equation of state (2) for R32

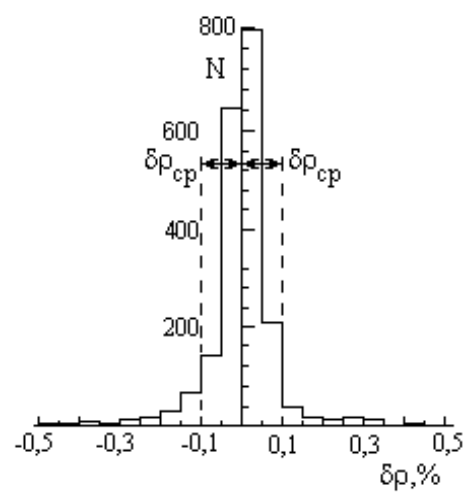
i	j	a_{ij}	i	j	b_{ij}
1	0	1.183486	1	4	-6.546357E-02
1	1	-2.430934	1	5	-2.784785E-01
1	4	-1.472179E-02	2	1	1.113400
2	0	-4.506743E-01	2	2	-2.954417
2	1	1.721527	2	4	4.898234
2	2	-1.349166	2	5	-2.354906
3	1	-6.052212E-01	3	5	-7.709682E-01
3	2	9.265910E-01	4	5	6.502963E-01
4	0	8.081905E-02	5	3	2.168338E-01
4	2	-1.999587E-01	5	4	-5.499117E-01
4	3	3.655934E-03	6	3	1.978099E-02
5	2	8.217181E-03	6	5	9.535163E-02
6	0	-3.230880E-03	8	4	-1.425744E-02
6	1	5.778584E-03	9	2	3.921874E-03
10	0	-2.536027E-06			

Table 3. Coefficients a_{ij} and b_{ij} of the equation of state (2) for R125

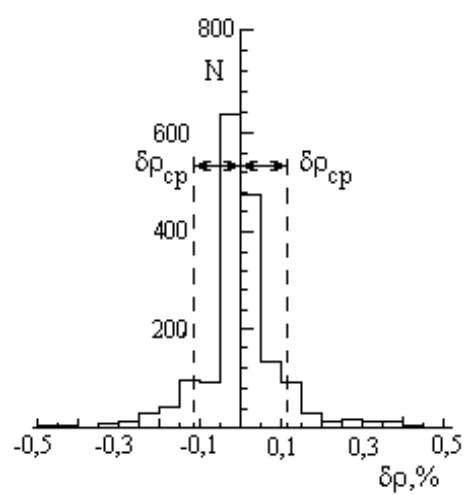
i	j	a_{ij}	i	j	b_{ij}
1	0	2.825627E-01	1	4	1.203782E-01
1	1	-6.854910E-01	2	1	1.687868E+01
1	3	-9.975127E-01	2	2	-6.643158E+01
2	1	6.445149E-01	2	3	9.473412E+01
2	3	4.024926E-01	2	4	-5.988361E+01
3	1	-7.060325E-01	2	5	1.396914E+01
4	2	2.621465E-01	3	2	6.765262E-01
5	0	1.118047E-01	4	1	-5.880934E-02
5	2	-1.217283E-01	4	3	-5.648372E-01
6	0	-3.381068E-02	5	4	1.643516E-01
7	1	7.828134E-03	6	1	6.900750E-01
7	2	2.074012E-03	6	2	-1.066543
7	4	-5.912590E-05	6	4	3.699827E-01
8	3	8.017074E-05	7	5	-4.472888E-02
10	1	-5.547434E-05	10	1	6.506423E-03
			10	3	-8.564364E-03

FIGURE CAPTIONS

Fig.1 Histograms of deviations δp for R32 (a) and R125 (b).



(a)



(b)